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A Device For Computer-Controlled Potential Modulation In Electrochemical Fourier Transform Infrared Spectroscopy

by

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A DEVICE FOR COMPUTER-CONTROLLED POTENTIAL MODULATION IN ELECTROCHEMICAL FOURIER TRANSFORM INFRARED SPECTROSCOPY

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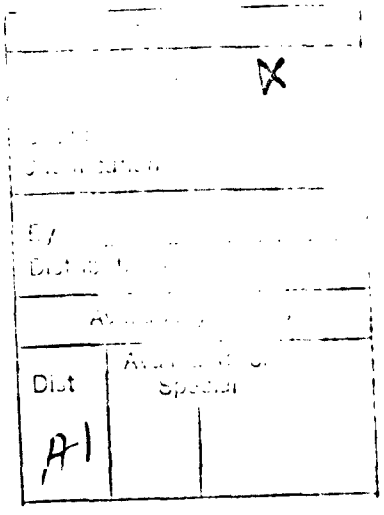
ABSTRACT

A circuit has been designed for the automatic control of potential modulation for subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) using an IBM IR/90 series FTIR spectrometer. This device enables the potential modulation to remain synchronized with the spectral data collection under all conditions.



Recently, the technique of subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) has provided a new approach to studying the *in-situ* vibrational properties of adsorbed electrochemical reactants and related species at metal-electrolyte interfaces.[1] The technique involves the alteration of the electrode potential between two values which define distinct states of the electrode surface. The electrode potential is held for a sufficient period at each potential to accumulate data from many scans of the interferometer and the two sets of data are then appropriately ratioed and subtracted. However, in order to obtain the desired sensitivity, a large number of scans, on the order of 500-2,000, are required at each potential. This results in a substantial amount of time being required to generate the difference spectra (ca. 20 minutes) and hence, the system is subject to a large drift in the baseline absorbance. This problem may be minimized, at least in instances where the species of interest is reversibly adsorbed, by modulating the potential between its reference and sample values periodically and repeating the step sequence until the desired number of scans has been accumulated.[2]

The device described here was developed so to reliably synchronize such potential modulation with the spectral data collection by utilizing the digital logic of FTIR spectrometers that normally drives the autosampler. Although the circuit was designed to be used with IBM FTIR instruments, specifically the IBM IR/90 series, the device presented herein may be readily adapted to any instrument that possesses the capability of controlling an autosampler via comput command.

Previous methods of potential modulation utilize the signal from one of the interferometer scan control lines (i.e., PRESET or START)

located within the optics bench.[2] The scan-control pulses are used to increment a digital counter whenever an interferometer scan has been completed. Once the desired number of scans has occurred, the potentiostat receives a trigger pulse from the counting circuit, resulting in an appropriate alteration in the electrode potential. Problems arise, however, if an interferogram cross-correlation routine is applied.

The purpose of such a routine is to determine how well a particular interferogram correlates with those obtained from preceding scans of the interferometer and to discard the scans that do not demonstrate the desired precision. Invariably there are several scans of the interferometer from which no data are taken on this basis, and hence they are not counted by the computer. Since the digital-counter system described above obtains its signal from the scan control lines, it is unable to distinguish if a scan has been accepted or ignored by the computer. Therefore, in the event that a scan is disregarded, the potential modulation will no longer be synchronized with the spectral data collection. Although it is possible to turn off the correlation routine so that the computer accepts every scan, this results in a reduction of the signal-to-noise ratio.

The circuit illustrated in the Figure provides a simple means of circumventing this difficulty. It utilizes instead circuitry which is normally available in FTIR spectrometers (as in the IBM IR 90-series employed here) to drive the autosampler, and therefore is controlled by a predetermined number of *successful*, rather than *total*, interferometer scans. Consequently, the delay between trigger pulses to the potentiostat will always correspond to a fixed number of successful scans, rather than to a fixed time delay, so that synchronization between the potential modulation and the data collection will consistently be maintained. No

permanent modifications to the instrument were necessary since all the necessary driving logic is included as standard equipment and the device is connected solely to plug C-8 (see Figure) which is located inside the optics bench and is normally reserved for an automatic sample changer.

The operation of the circuit is relatively straightforward. When the "sample position" (i.e., the value stored in the counter, IC-5) does not match the position selected by the autosampler circuitry, the 12 V supply is activated (PIN B). The counter is immediately reset and is then incremented until the count equals the desired value. Since only two sample positions are required, we select counter values of 0 and 1 so to minimize the elapsed time for this process (about 1 sec). When the desired count is achieved, the 12 V supply is deactivated and counting ceases. (Although only two positions are used to select the potential a four bit counter is necessary so that the spectrometer will continue to operate even if a sample position other than 1 or 0 is selected.) The resulting waveform (PIN 2, IC-6) is used to drive a suitable potentiostat, one for which switching between a pair of preset electrode potentials can be accomplished by means of such external pulses (for example, PAR Model 173).

This potential modulation device is simple to build and yet is very effective. By adjusting the electrode potential in this fashion via the system software one is not only assured that the potential modulation and the spectral data collection are synchronized but greater flexibility is also achieved. Thus this procedure makes is possible, through the use of a software routine, to implement time delays prior to the collection of data to allow the electrochemical system to stabilize. Such stablization may be required, for example, with systems displaying sluggish adsorption-desorption kinetics.

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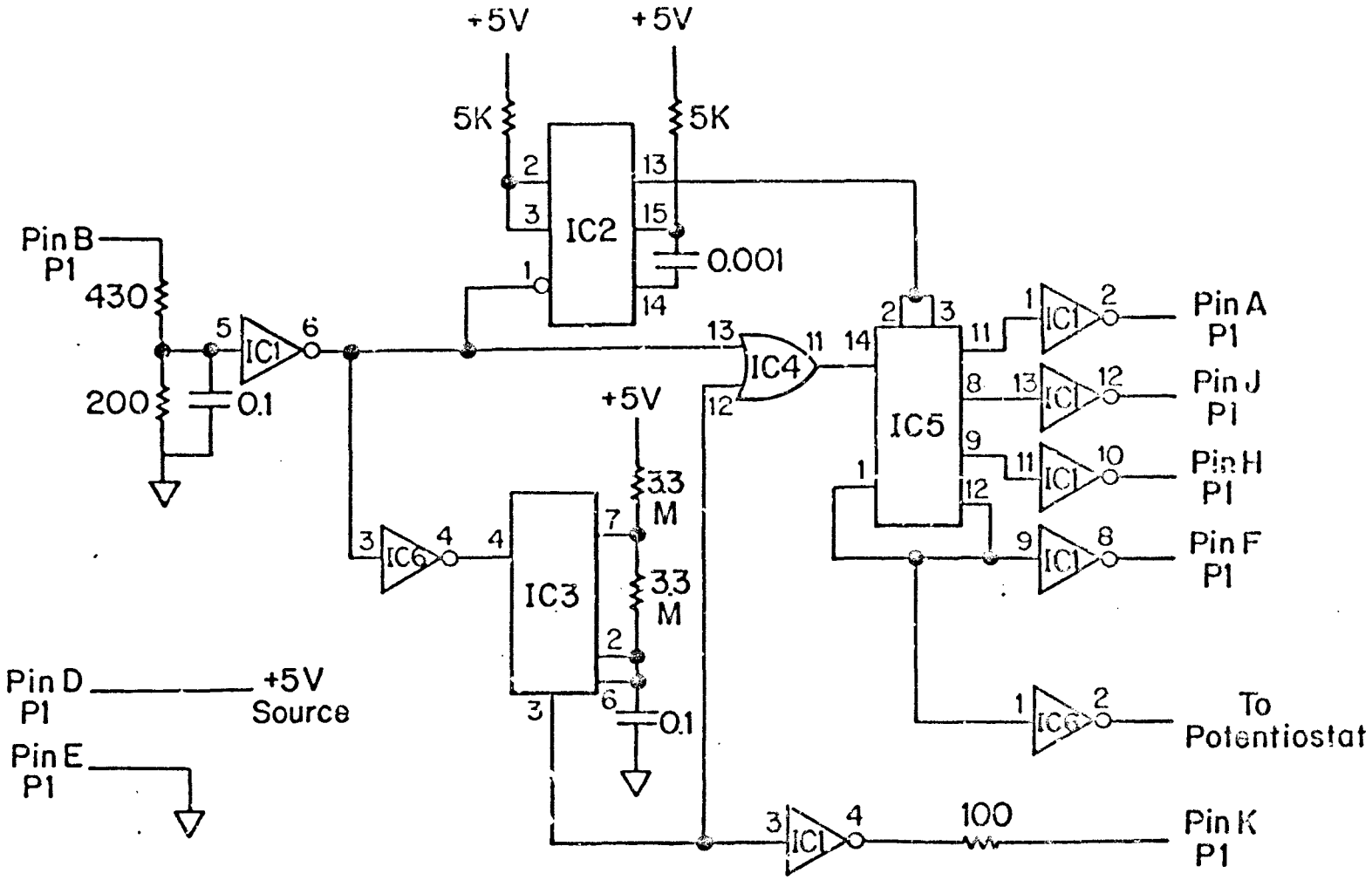
[1]S. Pons, J. Electroanal. Chem., 150, 494-504 (1983).

[2]S. Pons, T. Davidson, and A. Bewick, J. Electroanal. Chem., 160, 63-71 (1984).

Figure Caption

Schematic diagram of the Interface for computer-controlled synchronization of FTIR spectral scans and electrochemical potential modulation. IC1 = 7414; IC2 = 74123; IC3 = LM555; IC4 = 7432; IC5 = 7493; IC6 = 7404. All resistors 1/4 watt, C1 and C3 are ceramic disc capacitors and C2 is silver-mica. P1 is a 9 pin Hex plug (Amphenol #126-013) so to match with plug C8 in the optics bench. Power-supply connections for the integrated circuits have been omitted for clarity.


+5V
+5V
5K
5K
IC2
0.001
Pin B
P1
430
200
0.1
IC1
IC4
IC5
IC6
IC3
+5V
3.3
M
3.3
M
0.1
Pin D
P1
+5V
Source
Pin E
P1
100
Pin A
P1
Pin J
P1
Pin H
P1
Pin F
P1
To
Potentiostat
Pin K
P1

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